Title: DEEP DESULFURIZATION OF DIESEL FUEL BY A NOVEL INTEGRATED APPROACH

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ABSTRACT

OBJECTIVE

The overall objective of this project is to explore a new desulfurization system concept, which consists of efficient separation of the refractory sulfur compounds that constitute less than 500 ppmw of diesel fuel by selective adsorption, and effective hydrodesulfurization of the concentrated fraction of the refractory sulfur compounds in diesel fuels. In the present period of performance, our approaches focused on 1) modifying a flowing adsorption system for adsorption experiments; 2) screening different adsorbents; 3) measurements of capacity and selectivity of the adsorbents; 4) regenerating the spent adsorbents.

ACCOMPLISHEMENTS TO DATE

A flowing adsorption device has been modified in order to further increase the experimental efficiency. The modified device allows testing four adsorbent samples simultaneously with different LHSV at a temperature range from ambient temperature to 400 ˚C. The system includes HPLC pumps, a gas system, four adsorption columns in a furnace, and a sample collection system. The pretreatment of adsorbents and regeneration of spent adsorbents can also be conducted in the same device. A high temperature and high pressure reactor system was also set up for the pretreatment of adsorbents and regeneration of spent adsorbents, which can be run at a temperature range from ambient temperature to 800 ˚C and a pressure range from ambient pressure to 1000 psig.

Different types of the materials, including metals, metal oxides, metal sulfides with or without supporter, have been prepared and tested at a temperature range from ambient temperature to 250 ˚C for adsorption desulfurization of model diesel fuels and real diesel fuel. In terms of the adsorption capacity, a bulk transition metal-based adsorbent (A-2) and a supported transition metal based adsorbent (A-5) were found to be the two most promising adsorbents for selective adsorption desulfurization of liquid hydrocarbons. A-2 and A-5 exhibit the significant selectivity for sulfur compounds, such as alkyl benzothiophenes and dibenzothiophene (DBT) in diesel fuel. A-2 and A-5 can also selectively remove 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in real diesel fuel, although the adsorptive selectivity of 4-MDBT and 4,6-DMDBT is lower than that of DBT. The regeneration of the spent A-5 was explored by using hydrogen at higher temperature. The adsorptive performance of the regenerated A-5 is almost the same as that of the fresh A-5.

Some sulfur-containing metal- based adsorbents (A-6) show good adsorptive selectivity towards alkyl benzothiophenes, even 4,6-DMDBT, although the adsorptive capacity is less than those of A-2 and A-5. The adsorptive selectivity decreases in the order of DBT > 4-MDBT > 4,6-DMDBT, indicating that the methyl groups at the 4- and 6-positions inhibit the adsorption of alkyl DBTs. A significant advantage of A-6 is that the spent A-6 can be easy to regenerate by solvent washing followed by heating adsorbent bed to remove the solvent. The regeneration can be run at relative lower temperature and without using hydrogen. The preliminary adsorption experiments with a model diesel fuel indicate that the regenerated A-6 shows a performance similar to the fresh A-6.

A full US patent was filed by Penn State in February 2003 (a provisional US patent was filed in February 2002) on the selective adsorption for removing sulfur from liquid fuels. The filing of provisional and full US patent has been reported to DOE by Penn State Intellectual Property Office in 2002 and 2003, respectively.

FUTUER WORK

We will continue to improve the metal-sulfide-based adsorbents to increase their adsorptive capacity, as this type of the adsorbents is easy to be regenerated by solvent washing. We will optimize the regeneration process of the spent adsorbents, including the regeneration temperature, LHSV and selecting solvent. We will explore the adsorption mechanism of various sulfur compounds on different types of adsorbents by a combination of experimental and computational results.

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